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# The role of charge carriers in the memory effect in the incommensurate phase of the semiconducting ferroelectric $\text{Sn}_2\text{P}_2\text{Se}_6$

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**Abstract.** The memory effect in the incommensurate phase of the semiconducting ferroelectric  $\text{Sn}_2\text{P}_2\text{Se}_6$  is studied by dielectric measurements. The mechanism of the memory effect is associated with the pinning of the incommensurate modulation by a charged, most probably dipolar, defect density wave. It is suggested that a defect density wave is formed by a recharging of certain ions in the crystal lattice. The spatial distribution of the defects is defined by the population of trapping levels in the band gap.

Comparison of the shape and temperature behaviour of the memory effect anomaly with theory and additional experiments, such as measurement of the thermostimulated current and determination of the activation energy of the charge carriers by various techniques, showed that the memory effect for the most part originates in the modulated population of the charge carriers on trap levels in the band gap.

## 1. Introduction

One of the most fascinating non-equilibrium phenomena, characteristic of incommensurate systems, is the memory effect. If a crystal is kept in the incommensurate (IC) phase at a certain stable temperature  $T^*$  for a sufficiently long time, then, on passing this temperature again, anomalies of various physical properties are observed. This is caused by the formation of a phase with fixed wave vector within the IC phase, which becomes locked in a certain temperature region around  $T^*$  due to the pinning of the incommensurate modulation. The memory effect has been observed in various IC systems including proper and improper ferroelectrics [1, 2, 3]. It was most thoroughly studied in thiourea [2]. In all cases the effect has been attributed to the coupling of mobile defects to the modulation order parameter [4], forcing the defects to diffuse in the IC modulated potential. However, the nature of the defects remains unknown. Moreover, from an optical study of the memory effect in quartz it was concluded that in that case the mobile defects model cannot explain all of its features [5]. There it was assumed that the local reorientation of defects in the field of the IC wave plays an essential role in the mechanism of the memory effect.

Recently it has been shown that the memory effect in the semiconducting ferroelectric  $\text{Sn}_2\text{P}_2\text{Se}_6$  is significantly affected by light [6, 7]. This suggests a considerable role of charge carriers in the memory effect, and not the diffusion of mobile defects.

In the present paper we examine the role of these charge carriers and we will show that the memory effect is associated with a spatial inhomogeneous (modulated) filling of trap levels in the band gap with charge carriers. The investigations have been carried out using a dielectric technique.

$\text{Sn}_2\text{P}_2\text{Se}_6$  is one of the few proper ferroelectrics which show an incommensurate phase. Between the temperatures  $T_c = 193$  K and  $T_l = 221$  K an incommensurate phase is observed with an average structure of the high-temperature paraelectric phase with space group  $P2_1/c$  and a modulation vector  $q_z$  varying between  $0.08 c^*$  and  $0.071 c^*$ . At the lock-in phase transition at  $T_c$  the crystal becomes ferroelectric with space group  $Pc$ .

## 2. Experiment

The experiments have been carried out on two [100] oriented samples with typical size  $2 \times 2 \times 1$  mm<sup>3</sup> cut from the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystals grown using vapour transport and Bridgman techniques. Gold electrodes were evaporated on the (100) faces. The  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystals grown by these two methods differ essentially in electroconductivity. In particular, the Bridgman-type sample used in the experiment had a specific conductivity at room temperature of about  $10^{-10} \Omega^{-1} \text{ cm}^{-1}$ , while the conductivity of the vapour-transport-type sample was about  $10^{-7} \Omega^{-1} \text{ cm}^{-1}$ . Due to this difference in electroconductivity the influence of semiconducting properties on the memory effect could be investigated without incorporating undesirable effects usually connected with illumination of the sample, such as inhomogeneity of sample illumination and temperature gradients as well as a photoinduced space charge near the electrodes. In the following we shall only focus on the vapour transport crystal because the memory effect in the highly ohmic Bridgman-type crystals remained very weak even after keeping the sample at a stable temperature for a very long time of 15–17 h. In contrast, the vapour-type crystal exhibits pronounced anomalies in the vicinity of the stabilization temperature after keeping the sample at this temperature for a relatively short time of 10–15 min.

It should be noted that these two kinds of crystal differ noticeably also in other properties. For instance, the crystals of the Bridgman type exhibit a very large domain wall contribution to the dielectric constant below the lock-in phase transition, typical of proper ferroelectrics with an incommensurate phase. The domain wall contribution in vapour-transport-type crystals is much smaller. We suggest that the suppression of the domain wall contribution in these crystals is caused by internal electric fields induced in the course of spontaneous polarization screening or by pinning of the domain walls by space charges accumulating near the domain walls. Thermal expansion measurements on these two kinds of sample indicate that the quality of the Bridgman-type crystal is worse [8]. The observed deviation of thermal expansion around  $T_l$  from the Landau theory in this kind of crystal is suggested to be caused by random-field-type defects. Although the concentration of defects thus is expected to be larger, the memory effect in this kind of crystal is very weak.

The dielectric experiments were performed using a General-Radio 1615-A transformer bridge. A measuring frequency of 100 kHz was taken in order to suppress the observed contribution to the dielectric susceptibility of a low-frequency non-fundamental polarization mechanism, presumably caused by the so-called surface dielectric layers. The temperature of the samples was stabilized to within  $\pm 0.1$  K by an Oxford Instruments continuous flow cryostat for a long period of time. Continuous cooling (or heating) measurements were carried out at a temperature variation rate of approximately  $0.2 \text{ K min}^{-1}$ .

### 3. Results and discussion

In figure 1 the temperature dependence of the dielectric constant of the vapour transport  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal is shown in the vicinity of the stabilization temperature. After the (in this case two successive) temperature stabilizations (two) anomalies appear. The locations of the anomalies on the cooling and heating curves are shifted in temperature by the magnitude of the global temperature hysteresis (see inset of figure 1). The cooling of the sample down into the ferroelectric phase leaves the induced anomalies unaltered.

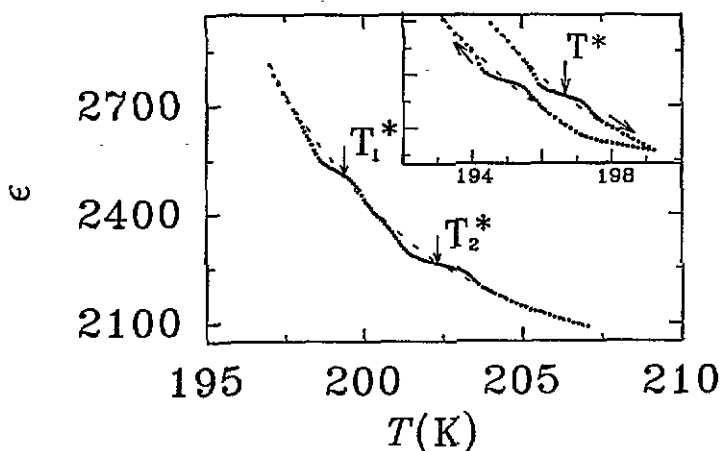


Figure 1. The memory effect in a dielectric measurement after two temperature stabilizations for 120 min on a heating curve. Inset: the memory effect in a dielectric measurement for the  $\text{Sn}_2\text{P}_2\text{Se}_6$  vapour-transport-type crystal after temperature stabilization at  $T^*$  on a heating curve for 120 min. The broken lines represent the regular behaviour of  $\epsilon$ .

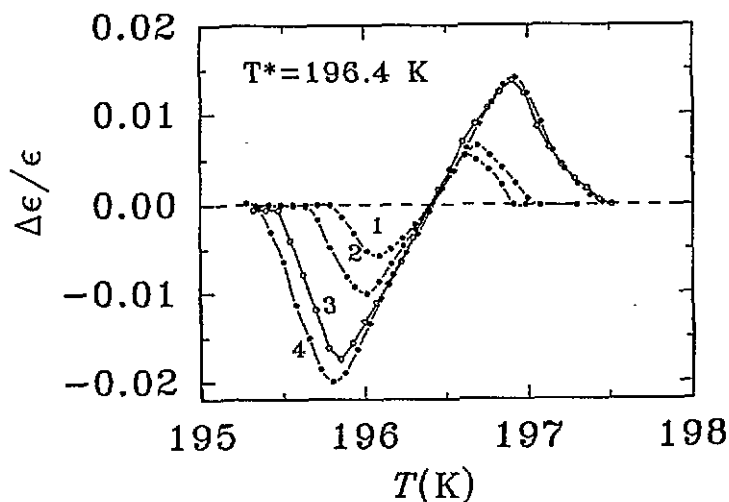


Figure 2. Temperature dependence of the reduced anomalous part of the dielectric susceptibility associated with the memory effect at various stabilization times ( $T^* = 196.4$  K). 1: 15 min; 2: 45 min; 3: 120 min; 4: 230 min.

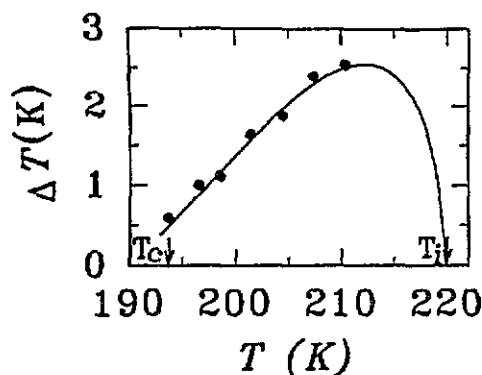


Figure 3. Dependence of the temperature interval  $\Delta T$  between the maximum and minimum of  $\Delta\epsilon/\epsilon$  on the stabilization temperature. The stabilization time was 120 min. The solid line is a fit obtained with equation (4).

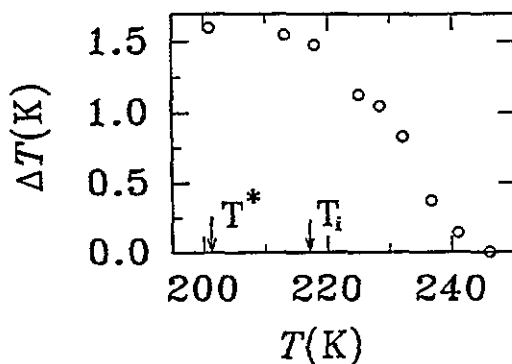


Figure 4. The variation of the width of the locked phase on heating the sample above the stabilization temperature.

In figure 2 the temperature dependences of the relative anomalous parts of the dielectric susceptibility associated with the memory effect are presented for several stabilization times. It is obvious that the amplitude and the width of the anomaly grow with an increase in stabilization time.

Further, upon increase in stabilization temperature, the temperature interval  $\Delta T$  between the minimum and maximum of  $\Delta\epsilon/\epsilon(T)$  shows an increase (figure 3). It should be mentioned that, because of high dielectric losses at  $T \geq 212$  K, it was impossible to trace this temperature variation up to the IC phase transition ( $T_i$ ).

Heating the sample within the IC phase up to  $T_i$  leaves the memory effect anomaly almost unaltered. However an increase in temperature above  $T_i$  is accompanied by a gradual suppression of the memory effect anomaly. Finally, heating the crystal above approximately 245 K results in a complete disappearance of the memory effect (figure 4).

The fact that the memory effect is susceptible to the illumination of the sample [6, 7] as well as the fact that it is much larger in weakly ohmic than in highly ohmic  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystals, suggests that charge carriers play a dominant role in the memory effect in the crystal studied. One can assume that in the course of the trapping of the charge carriers a periodical distribution of charged defects is produced.

In order to examine the role of the charge carriers in the mechanism of the memory

effect in more detail we have used a thermally stimulated current technique in the following ways. In one case the sample has been cooled down from temperatures around 250 K into the ferroelectric phase in the presence of an applied electric field of  $0.8 \text{ V cm}^{-1}$ . Thereafter, removing the electric field, the sample was connected to an electrometer (Keithley model 616) and the depolarization current was recorded using a fixed heating rate of about  $10 \text{ K min}^{-1}$ . In the circuit of the sample, along with the pyroelectric current observed in the ferroelectric phase, a thermally stimulated current flows above  $T_c$ , changing its sign within the IC phase, going through the highest maximum in the vicinity of  $T_i$  and passing another maximum at temperatures around 230 K (see figure 5, curve 1). In the other case the sample was cooled down from 250 K in the presence of an applied electric field only into the low-temperature region of the incommensurate phase. The thermally stimulated current in this case is characterized by only one, not very strong maximum, localized within the IC phase (curve 2 in figure 5). Thus we notice that the maximum of the thermally stimulated current at approximately 230 K only occurs in the case when the sample is cooled down into the ferroelectric phase. Therefore one can conclude that its nature is not only connected with a spatial redistribution of the charge carriers on the traps under the effect of the external bias field. If this were the case, the maximum of the thermally stimulated current would also be observed after cooling the sample under the bias field only into the IC phase. Thus, it follows from these results that the created polarization,

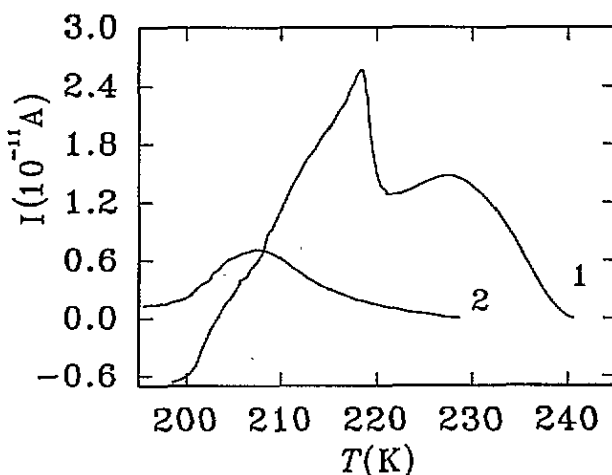


Figure 5. Temperature dependences of the thermally stimulated current for two different polarization regimes. Curve 1 was obtained after cooling the sample under the bias field into the ferroelectric phase; curve 2 was obtained after cooling the sample into the incommensurate phase.

responsible for the peak of thermally stimulated current at 230 K, has an intrinsic nature, associated with the spontaneous ferroelectric polarization.

In the case of the incommensurate phase, because of the modulated distribution of the spontaneous polarization in the IC phase, the net induced polarization in the sample is virtually zero. Therefore, this polarization does not manifest itself in the thermally stimulated current. The maximum on curve 2 in figure 5 and the corresponding weak shoulder in the same temperature range on curve 1 are suggested to be related to the polarization induced by the external bias field.

Thus from the above discussion it can be concluded that under the influence of the

spontaneous polarization an electronic polarization is induced in the crystal.

Notice that the curves of thermally stimulated current are rather reproducible, provided that the polarization conditions (voltage across the sample, cooling rate) as well as measuring conditions (heating rate) are the same.

These results from the thermally stimulated current strongly favour the idea of an electronic nature of the memory effect in  $\text{Sn}_2\text{P}_2\text{Se}_6$ . The peak in curve 1 in figure 5 at approximately 230 K corresponds to that temperature, heating above which leads to an abrupt suppression of the memory effect anomaly (figure 4). Moreover the thermally stimulated current disappears completely around 240 K, which coincides with that temperature on heating above which the anomaly vanishes. Unfortunately, because of the presence of the strong maximum around the  $T_i$  on the temperature dependence of the thermally stimulated current it is not possible to determine the activation energy of the local centre responsible for the high-temperature maximum.

The presence of a polar direction in the crystal implies that the shape of the potential for the spatial distribution of charge carriers on the trap levels is asymmetric. A number of effects such as the photovoltaic effect, relaxation currents and even electroconductivity result from an asymmetry of excitation of charge carriers in polar materials [9]. Due to the asymmetry a difference in population of the levels appears: the probability of excitation of charge carriers along the polarization vector and opposed to it are different. Therefore the modulated spontaneous polarization in the IC phase can give rise to a modulated redistribution of charge carriers on the trap levels. The theory of the memory effect caused by these trapped charge carriers has been elaborated in [10]. The principle of this model is based on the appearance of an inhomogeneous density of carriers on the trap levels due to the modulation of the energy of the local centre in the band gap. The density of electrons at the trap levels is defined by a homogeneous  $m_0$  and an inhomogeneous component  $m_1$ :  $m = m_0 + m_1(z)$ . The inhomogeneous density  $m_1$  is described by

$$m_1 \approx \frac{N_c \exp(-U_0/kT) a m_0 / kT}{n_0 + N_c \exp(-U_0/kT)} P_q^2 \quad (1)$$

where  $n_0$  is the density of the conduction electrons,  $N_c$  is the density of states in the conduction band and  $a$  is the coefficient in the expression  $U = U_0 + a P_q^2$ , which describes the dependence of the interval between the bottom of the conduction band and trap levels on the order parameter  $P_q$ .

Without going into the details of the microscopical nature of the electronic polarization we will assume the coupling potential between the modulation order parameter ( $P_q$ ) and the electronic induced polarization ( $P_{in}$ ) to be linear. Let us present  $P_{in}$  in the form  $P_{in} = m_1(z) P_0$ , where  $m_1(z)$  is the density of the electrons trapped by the local centres given by (1) and  $P_0$  is the effective dipole moment of the recharged centres. Following [2] the coupling potential can be written as

$$V = V_0 m(z) P_0 P_q \delta(q q^*) \quad (2)$$

where  $q^* = q(T^*)$  corresponds to the wave number of the sinusoidal modulation of the induced electronic polarization. The coupling potential between the modulation order parameter and the electronic polarization induced during the 'writing time' of the memory effect can be considered as an Umklapp term. In such an event the temperature interval within which the wave number  $q^*$  is locked is given by [2]

$$\Delta T = \frac{\sqrt{2} (V P_q^{-2})^{1/2}}{\pi \alpha^{1/2} \zeta} \quad (3)$$

where  $\zeta = (dq/dT)|_{q=q^*}$  and  $\alpha$  is the coefficient in the  $(\alpha/2)(dP_x/dz)^2$  gradient term in the expansion of the thermodynamic potential [12]. Inserting the expressions for the coupling potential (equation (2)) and the density of charge carriers on the trap level (equation (1)) into equation (3),  $\Delta T$  is expressed by

$$\Delta T = \frac{\sqrt{2}}{\pi \alpha^{1/2} \zeta} \frac{(V_0 N_c \exp(-U_0/kT) a m_0 P_q / kT)^{1/2}}{n_0 + N_c \exp(-U_0/kT)}. \quad (4)$$

In this formula the time dependence of the density of the recharged centres has not been taken into account. It is assumed that  $P_q \sim (T_i - T)^{1/2}$ . A fit of (4) to the experimental temperature dependence of  $\Delta T$  gives  $U_0 = 0.42 \pm 0.01$  eV,  $N_c = 1 \times 10^{19} \text{ cm}^{-3}$  and  $n_0 = 8.9 \times 10^9 \text{ cm}^{-3}$  as parameters. The magnitudes of  $N_c$  and  $n_0$  are quite reasonable for wide-band-gap semiconductors. In particular, the parameters obtained coincide very closely in magnitude with those used in [10] for theoretical estimates. From the temperature dependence of the electroconductivity on bias field at  $T > T_i$ , the activation energy  $U_0$  was found to be approximately 0.36 eV.

The estimate of the activation energy from DC electroconductivity in semiconducting ferroelectrics might deviate because of presence of highly ohmic surface layers characteristic of these kinds of material [11]. In order to avoid this problem we have additionally estimated the activation energy of the local centres from temperature-frequency measurements of the complex dielectric constant.

The frequency measurements have been performed using the General-Radio 1615-A transformer bridge at a measuring voltage of about  $3 \text{ V cm}^{-1}$  in the frequency region from 50 Hz to 100 kHz. Above the lock-in phase transition the dielectric constant exhibits a dispersion spread in a wide frequency region. With increasing temperature, the real part of the dielectric constant at certain fixed frequency shows an increase. Simultaneously, the temperature dependence of the imaginary part of  $\epsilon$  exhibits a maximum. This maximum shifts upward as the measuring frequency increases. The frequency dependence of  $\epsilon'$  and  $\epsilon''$  also shows a behaviour characteristic of a relaxation dispersion. The character of the dispersion allows us to relate it to the presence of surface layers, characteristic of semiconducting ferroelectrics. The equivalent circuit of such a sample can be presented as a sequence of three capacitors with losses. The frequency dependence of the complex dielectric constant of such a system is similar to a Debye-type dispersion, with the exception that  $\epsilon''$  increases with decreasing frequency [13]. By assuming an Arrhenius-type behaviour for the relaxation frequency ( $\omega = \omega_0 \exp(-U/kT)$ ) the activation energy can be determined from its temperature dependence. The relaxation frequency can be determined from the maxima of the  $\epsilon''$  at various measuring frequencies.

It should be mentioned that the relaxation frequency for such a three-capacitor equivalent circuit is inversely proportional to the resistance of the bulk of the sample, provided that the resistance of the surface layers is much larger than the resistance of the bulk and the capacitance of all capacitors does not change too much with temperature.

A fit of the temperature dependence of the relaxation time to the Arrhenius equation gives an activation energy of the relaxation process  $U_0 \approx 0.41$  eV (figure 6). This energy can be attributed to the energy of the local centre which defines the electroconductivity at given temperatures. The deduced value is in good agreement with the energy of the local centre evaluated by fitting of the experimental data of  $\Delta T$  to equation (4).

In the close vicinity of  $T_i$   $\Delta T$  calculated using equation (4) shows a drop (figure 3). Evidently this is caused by the temperature dependence of  $P_q$  which tends to zero as  $T_i$  is approached.

As can be seen from figure 7,  $\Delta T$  tends to saturation with an increase in the temperature



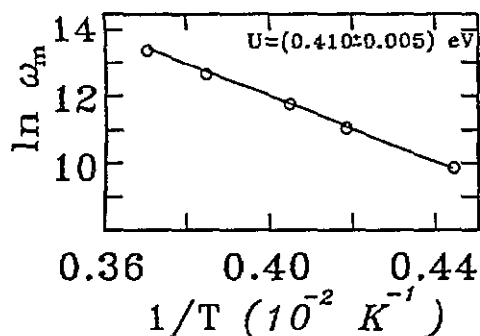


Figure 6. The relaxation frequency of the dielectric dispersion as a function of  $1/T$  ( $\omega_m$  was determined from the maxima of  $\epsilon''$ ). The solid line is a fit to the Arrhenius equation.

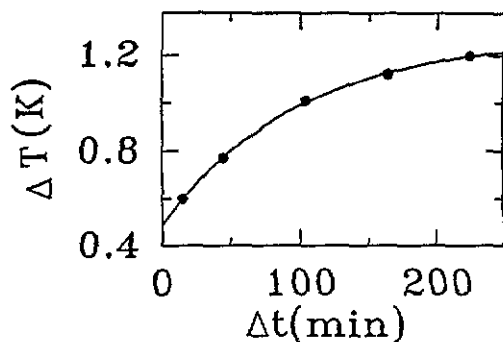


Figure 7. Dependence of the temperature interval  $\Delta T$  between the maximum and minimum of the  $\Delta\epsilon/\epsilon$  on the stabilization time ( $T^* = 196.5$  K).

stabilization time interval. The solid line in figure 7 is a fit to an exponential variation of  $\Delta T = 0.49 + 0.79(1 - \exp(-t/\tau))$  with  $\tau = 101 \pm 8$  min. According to our model, in which the memory effect is related to the inhomogeneous distribution of charge carriers on the trap levels, the time constant  $\tau$  can be attributed to the charge carrier relaxation on the trap levels. This time relaxation is determined by the following equation

$$\tau = (\gamma_n(n_0 + N_c \exp(-U_0/kT)))^{-1} \quad (5)$$

where  $\gamma_n$  is the kinetic coefficient [10]. Using  $n_0 = 8.9 \times 10^9 \text{ cm}^{-3}$ ,  $N_c = 1 \times 10^{19} \text{ cm}^{-3}$  and  $U_0 = 0.42 \text{ eV}$ ,  $T = 196.5 \text{ K}$  and  $\gamma_n = 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  (typical for wide-band-gap semiconductors [10]),  $\tau$  is found to be equal to about 140 min. This value is in reasonably good agreement with that obtained from the dependence of  $\Delta T$  on writing time. As can be seen from figure 7 the fit of the  $\Delta T$  (K) gives a finite value of  $\Delta T$  at  $\Delta t \rightarrow 0$ . Similar behaviour has recently been observed in quartz [5]. In our opinion the origin of this effect in  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystals may be the presence of some shallower levels, which are characterized by relaxation times much smaller than that for the level with  $U_0 \approx 0.40 \text{ eV}$ .

It should be noted that, in the case of a defect mechanism of the memory effect, the defect concentration providing the pinning of the incommensurate modulation with a wavelength of 12–15 elementary cells should be very large: of the order of  $10^{20}$ – $10^{21} \text{ cm}^{-3}$ . Such concentrations are only tolerable for 'proper defects' of the crystal lattice. The recharging of the ions may be one of the mechanisms in creating this kind of defect. In the case of the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystals one can assume the following mechanism. Through the electron–phonon coupling the free charge carriers are localized near the  $(\text{P}_2\text{Se}_6)^{4-}$  anion quasimolecular groups, creating quasiparticles similar to the polaron. However, this is only one of the possible configurations which can be generated in the crystal by the recharging effect. Some evidence of the influence of the electronic subsystem on the memory effect has been mentioned even in pure dielectric materials, particularly in the  $[\text{N}(\text{CH}_3)_4]_2\text{CoCl}_4$  crystal [14]. Thus it is not improbable that similar kinds of electronic defect responsible for the memory effect are rather common for dielectric materials. To prove this suggestion additional investigations on different materials are required.

Let us finally consider in detail the dielectric anomaly due to the memory effect. As suggested in the theory [2] the  $q$  vector is locked at a certain modulation vector  $q^*$  corresponding to the stabilization temperature and left unchanged in some temperature

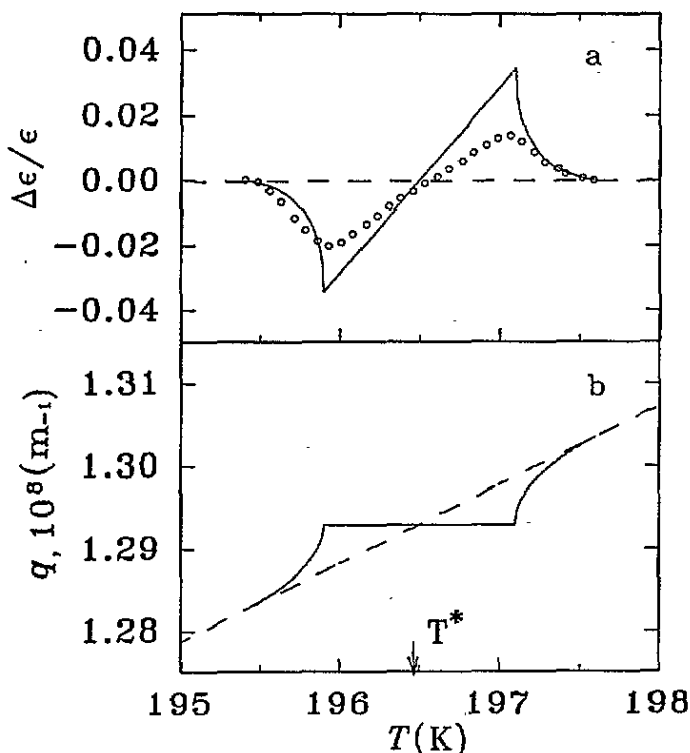


Figure 8. (a) Comparison between the experimental (open circles) and calculated (equation (5)) (full line) memory effect anomalies. (b) Schematic representation of the behaviour of the  $q$  vector of incommensurate modulation in the vicinity of the locked phase (for a description see the text). The dashed line corresponds to the experimental temperature dependence of the  $q$  vector.

region. Figure 8(b) represents schematically the behaviour of the  $q$  vector in the vicinity of the locked phase. Similarly to in [2] it is supposed that  $q(T)$  varies upon approaching the temperatures  $T_e$  limiting the locked phase according to the law  $q(T) - q^* \simeq \beta(T - T_e)^{1/2}$ . The width of the locked phase  $\Delta T$  was defined as the temperature interval between the minimum and maximum of the  $\Delta\epsilon/\epsilon$  (figure 2). Using

$$\frac{\Delta\epsilon}{\epsilon} = - \left( \frac{\xi}{\xi + 1} \right)^2 \left( \frac{T - T_0}{T_i - T} + \frac{\xi + 2}{\xi + 1} \right)^{-1} \frac{dq}{q} \quad (6)$$

( $\xi = 4/3\eta q^2 B$ ) obtained on the basis of the Landau–Ginzburg free energy expansion [2] (where  $B$  and  $\eta$  are the coefficients in the  $(1/4)BP_x^4$  and  $(\eta/2)(\delta P_x/\delta z)^2 P_x^2$  terms, respectively) the  $\Delta\epsilon/\epsilon$  function has been calculated. The parameters  $T_0 = 198$  K,  $\eta = 2.8 \times 10^{-8} \text{ J m}^7 \text{ C}^{-4}$ ,  $B = 3.2 \times 10^9 \text{ J m}^5 \text{ C}^4$  are taken from [12]. Equation (6) has been obtained for the case of positive  $\beta$ , that is when the  $(\gamma/6)P^6$  term in the free energy expansion is neglected. It is assumed that the result of the calculation is not significantly effected by this simplification. The experimentally determined temperature dependence of  $q$  was taken from [15]. The results are shown in figure 8, indicating that the theoretical dielectric anomaly qualitatively agrees with the experimental behaviour, within an order of magnitude. The occurring quantitative discrepancy may be caused by the following factors. First, some contribution to the dielectric susceptibility in the studied  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal is

made by the non-fundamental polarization mechanism not accounted for in the applied theory. Secondly, the coefficients  $\eta$  and  $B$  (taken from [12]) used for the calculations can be considered as estimates. Nevertheless the derived result indicates that the theory is valid and that the parameters used for the calculations are quite reasonable.

#### 4. Conclusion

The memory effect in incommensurate systems has always been associated with a periodic modulation of defect concentration (a defect density wave). However the nature of the defects and consequently the mechanism of the formation of the defect density wave are not entirely known. We have revealed that charge carriers play a crucial role in the mechanism of the memory effect in  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystals. The memory effect is described by a model based on coupling of the IC modulation to the defect density wave [2]. The mechanism of the defect density wave formation is attributed to the recharging of ions in the crystal lattice. Since the energy level of recharging ions is a quadratic function in the order parameter (in our case of the polarization), it is evident that the spatial distribution of the recharging ions is defined by the spatial distribution of the polarization.

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